96334EP

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
10 October 2002 (10.10.2002)

PCT

(10) International Publication Number
WO 02/080620 A1

(51) International Patent Classification⁷: H05B 3/14

(21) International Application Number: PCT/IB02/01024

(22) International Filing Date: 28 March 2002 (28.03.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01810314.3 28 March 2001 (28.03.2001) EP
01810675.7 9 July 2001 (09.07.2001) EP

(71) Applicant *(for all designated States except US)*: **ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE (EPFL)** [CH/CH]; Ecublens, CH-1015 Lausanne (CH).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **POLLIEN, Arnaud** [CH/CH]; Chemin Hemmerling 10, CH-1804 Corsier (CH). **LEDERMANN, Nicolas** [CH/CH]; St. Bonnet, CH-1195 Dully (CH). **BABOROWSKI, Jacek** [PL/CH]; Rue du Centre 44A, ch-1025 St. Sulpice (CH). **MURALT, Paul** [CH/CH]; Chemin du Record 18, CH-1315 La Sarraz (CH).

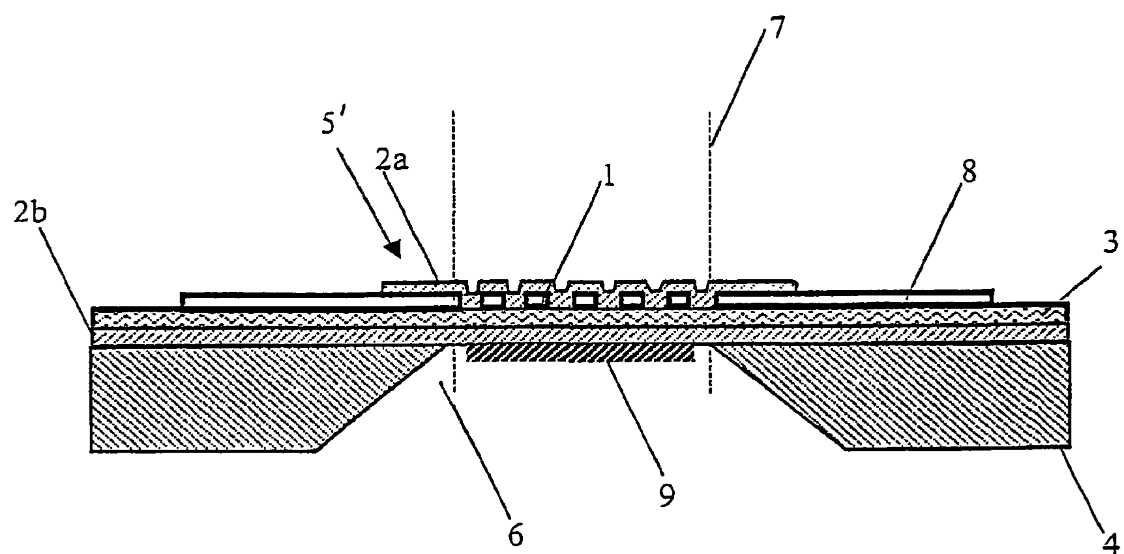
(74) Agent: **CRONIN, Brian**; Cronin Intellectual Property, Route de Clémenty 62, CH-1260 Nyon (CH).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

*[Continued on next page]*

(54) Title: HIGH TEMPERATURE MICRO-HOTPLATE




**(57) Abstract:** A micro-hotplate device, useful in catalytic high-temperature chemical sensors, micro-chemical reactors and as infra-red source, in particular at temperatures above 600° C, comprises a thin film resistive heater (1) made of a refractory metal silicide selected from silicides of tantalum, zirconium, tungsten, molybdenum, niobium and hafnium, the silicide having a polycrystalline structure obtainalble at temperatures above 600° C. The thin film resistive heater (1) is encapsulated between insulating layers (2a, 2b) forming a sandwich structure (5) and is located in a membrane (7) over an aperture (6) in a silicon substrate (4). The device is producible by standard micromachining techniques.

WO 02/080620 A1

**Published:**
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

# High Temperature Micro-Hotplate

## Field of the Invention

This invention relates to a micro-hotplate device comprising a thin film resistive heater, useful in catalytic high-temperature chemical sensors, micro-chemical reactors, micro-hot-fuel-cells and as infra-red sources, mostly as part of chemical sensors.

## Background of the Invention

Micro-hotplates are typically silicon micromachined elements produced using commercial silicon micromachining techniques together with bulk micromachining techniques in a batch process on a complete wafer, separable into individual elements by dicing. Such IR sources can be miniaturised - most IR micro sources measure only a few millimeters, typically of the order of 1-5 $mm^2$, but at least 0.01 $mm^2$ and at most 25 $mm^2$.

Micro-hotplates are parts of microsystems and have as function to heat a region of the device to several hundreds of degrees Celsius.

They can be equipped with an IR emission layer to radiate efficiently infrared light.

When provided with a catalytic layer containing noble metal such as Pt and Pd, they can be used as efficient catalytic devices, that can be provided with suitable templates to produce chemical reactions of the type liquid-solid, solid-solid or gas-solid for synthesis of materials *in situ*.

In catalytic sensors ("Pellistors") temperatures of 500 to 800°C are required. Infrared sources need about the same operating temperatures.

There is a wide range of application for a small, efficient and cheap infrared light emitter.

For instance, photoacoustic gas detectors are based on the principle that a gas irradiated by IR light absorbs it and is heated. The temperature increase leads to a pressure increase in the chamber. Pressure variations are measured by an acoustic detector or pressure sensor. Each kind of molecule has its specific absorption bands and for selective sensing, the infrared light is filtered. Combining a micro IR detector with an efficient infrared light micro source and the appropriate optics would allow the fabrication of a small and cost effective infrared spectrometer that could be used for gas analysis.

In this context, potential advantages of an infrared light micro source are numerous: high radiation density linked to the small size of the source; low power consumption; integration in miniaturised devices; no need for vacuum environment or encapsulation; and low cost of fabrication.

The principle of heating micro-hotplates relies on the Joule effect in a thin film resistor obtained by the deposition of a thin film of resistive material patterned by standard photolithographic techniques.

The crucial issue is the thermal stability of the resistive material and its interfaces. Most of the metals tend to form insulating oxides at high temperature, and the maximum achievable temperatures are greatly limited by the performance of such metal films. Moreover, there is a risk that the interfaces to silicon nitride and oxide become unstable due to silicide formation with the metal yielding material phases of uncontrolled compositions and properties.

A known, though partial solution to the problem is

the use of platinum films. Platinum does not oxidise even at high temperatures. However, platinum becomes mechanically unstable at about 500°C, above which atomic diffusion along surfaces and grain boundaries sets in to relax mechanical stresses. With electromigration, areas of higher current density - and thus higher temperature - tend to get thinner, leading to the formation of hot spots and finally to a break-up of the electrical conductor. This phenomenon can be partially suppressed by covering the patterned platinum film with an oxide, hindering interface diffusion. The application temperature can be increased to about 600°C by this measure.

Present IR light emitters often use a thin platinum film supported on a thermally and electrically insulating membrane, for example silicon dioxide and silicon nitride, on a silicon substrate. Because of the very good thermal insulation of the membrane, the IR source needs a low electrical power to reach the nominal temperature, typically 50-100 mW to reach a filament temperature of 500°C. See for example EP-A-0 689 229; US 5844676; and EP-A-0 776 023.

US patents 4,754,141 and 4,288,776 report that heavily doped single crystal silicon beam heaters covered with a $SiO_2$ film allow a working temperature of 800°C.

Polysilicon filaments are also reported to allow a filament temperature of 1000°C, see US Patent 4,609,903, but this kind of free standing structure only permits very small heating surfaces. Furthermore, as silicon is a very good heat conductor, such structure requires a high electric input power, as heat is lost by conduction through the heating filament. Further examples of micro-hotplate devices using a polysilicon heating element are described in US patents 5,345,213 and 5,464,966.

US patent 5,827,438 describes a thermal radiant

source forming a layered micro-hotplate structure having an incandescent layer made from metals such as tungsten, titanium-tungsten, tantalum or molybdenum.

In US patent 3,875,413 an infrared radiation source was proposed using a thin film resistor structure on a non-micromachined planar substrate of low thermal conductivity made of sapphire, $Y_2O_3$ or quartz of macrodimensions (measuring about 38mm x 5mm) and possibly coated underneath with a metal to prevent emission of spurious radiation. In order to restrict the hot zone in the central part of the device, the conducting structure was made of a high resistive material in the center and a well conducting material in the outer part. As high resistive material the transition metal silicide $Cr_3Si$ was proposed, which was known at that time as a thin film resistor material, and was selected because of its good absorption coefficient. The source was reported to work up to 700°C and was claimed to provide certain improvements over comparative heaters previously used for macrodimension infrared radiation sources with tungsten filament or ribbon as resistor material.

US Patent 6,091,050 proposes a heating platform for use at moderate temperatures, having a thermal contact using two layers of different thermal expansion that acts against a major surface of the device by a thermal bimetal effect. Aluminium serves as metal with high thermal expansion, and tantalum silicide (TaSi2) as material with low thermal expansion. The same bimetal layer is also used as resistive heater element. In this patent, the TaSi2 must not be heated above 300°C, which is well below the crystallisation temperature. Consequently, the TaSi2 is in its amorphous form which has a suitable low thermal expansion coefficient at ambient temperature at which the platform is to be used. Use of this device above 300°C is not contemplated. Moreover, applications at even higher temperature would

be impractical due to the fact that aluminium becomes unstable below 600°C.

In high temperature applications to which the present invention is directed, in order for the IR source to radiate as much IR light as possible for a given temperature and radiating surface, an emission layer is needed, such as black metal protected with a passivation layer. Known black layers such as black gold and black platinum degrade above 400° and 550°C, respectively, which limits their use.

Improving the maximum service temperature (T) of micro infrared light sources would provide a dramatic increase in the radiated power, as the latter is a function of $T^4$, according to the Stefan-Boltzmann law. This would improve the signal to noise ratio and thus increase the sensitivity and accuracy of gas detection.

## Summary of the Invention

An object of the invention is to develop a new thin film material to be used for the electrically conductive micromachined filament of an infrared light micro source that should be able to work at a temperature of 800°C or more, possibly with the oxidation resistance improved by a barrier layer.

The invention provides a micro-hotplate device comprising a thin film resistive heater made of a refractory metal silicide of polycrystalline structure, selected from silicides of tantalum, zirconium, tungsten, molybdenum, niobium and hafnium. This polycrystalline structure is obtainable at a temperature above 600°C.

In contrast to the amorphous tantalum silicide of US Patent 6,091,050, polycrystalline refractory silicides exhibit high melting points yielding a high thermal stability. They have melting points around 2000°C or

above and formation temperatures exceeding 600°C. They do not show diffusion and recrystallisation up to at least 900°C, and do not react with silicon. Being already silicides, no silicidation occurs with other silicon parts of the device.

These polycrystalline refractory silicides are thus stable as a function of temperature when placed in a structure adjacent to silicon-containing layers, making them ideal for incorporation into silicon semiconductor processing techniques for batch production. There is no driving force for the refractory silicides to alloy with silicon, leading to stable structures.

They also have high electrical conductivity, even at ambient temperature, and good high temperature mechanical properties: creep resistance and high melting temperature, as well as no recrystallisation or other morphological variation at high temperature, low atomic mobility and resistance to electromigration. They are compatible with the environment and with other materials, and have good resistance to oxidation in air at high temperatures, which can if necessary be improved by using a good oxidation barrier. Moreover, they have low stress in the temperature range considered; their thermal coefficient of expansion (about 10ppm/K) being similar to that of $SiO_2$ and $Si_3N_4$. Furthermore, they are compatible with standard silicon microfabrication processes, and can be deposited as a thin film and if required patterned to produce desired filament structures.

Crystalline phases of the refractory silicides are chosen as being most stable, avoiding unstable amorphous phases. However, it is acceptable to include up to about 5% by weight of amorphous material, located essentially at the crystalline grain boundaries and interfaces.

The selected polycrystalline refractory metal silicides offer improved high temperature stability

compared to the transition metal silicides of titanium, chromium and cobalt. It is known that bulk diffusion in metals and alloys occurs above roughly 0.5 of the absolute temperature of the melting point temperature. In this context, the critical temperature of, say, tantalum silicide compounds should be about 300°C higher than for $Cr_3Si$.

Preferably, the polycrystalline refractory metal silicide is protected from oxidation by a protective layer of material having low diffusibility for oxygen or oxygen vacancies, for example made of an oxide of tantalum, silicon or aluminium such as $Ta_2O_5$, $SiO_2$ or $Al_2O_3$. Materials like $ZrO_2$, which do not act as a barrier to oxygen, should be avoided. The listed materials form barrier layers providing excellent protection against oxidation during high temperature operation, whereby the devices can be used at temperatures up to or exceeding 800°C, even up to or above 1000°C.

As mentioned above, increasing the maximum service temperature of the micro-hotplate dramatically increases the radiated power, as the latter is a function of $T^4$, according to the Stefan-Boltzmann law.

The thin film resistive heater of polycrystalline refractory metal silicide is preferably encapsulated between insulating layers on a silicon substrate or wafer, using semiconductor batch processing wherein many devices are produced in one process on one or several substrates or wafers, then separated by micromachining techniques. Each individual resistive heater typically measures of the order of 1-5mm$^2$.

Manufacture of these micro-hotplates by standard CMOS processes provides advantages including low cost, and easy integration of VLSI circuits for drive, communication and control. The micro-hotplates can be easily incorporated into arrays of micro-hotplates each

with individualized circuits for control and sensing for independent operation.

The silicon substrate typically has a micromachined recess through which the bottom insulating layer is exposed, the sandwich structure forming a membrane traversing the recess on the silicon substrate.

Particularly when the sandwich structure forms a membrane supported over a recess in the substrate, the sandwich structure is mechanically reinforced by a ceramic supporting layer, such as $Si_3N_4$ or low stress silicon nitride, between the bottom protective layer and the thin film resistive heater.

The thin film resistive heater can be formed by a meander or other patterned layer in a membrane supported on a substrate, the membrane constituting a hot part of the device and the substrate constituting a cold part of the device. This patterned layer provides a given electrical resistance and optimises thermal conductance between the membrane and the substrate.

The polycrystalline refractory metal silicide typically comprises from 25 to 67 atomic % silicon, and can be selected from the following silicides of the given metals:

| | |
|---|---|
| Tantalum: | $Ta_3Si$, $Ta_2Si$, $Ta_5Si_3$, $TaSi_2$ |
| Zirconium: | $ZrSi_2$, $ZrSi$, $Zr_5Si_4$, $Zr_3Si_2$, $Zr_2Si$ |
| Tungsten: | $WSi_2$, $W_5Si_3$ |
| Molybdenum: | $Mo_3Si$, $Mo_5Si_3$, $MoSi_2$ |
| Niobium: | $Nb_5Si_3$, $NbSi_2$ |
| Hafnium: | $Hf_2Si$, $Hf_3Si_2$, $Hf_5Si_4$, $HfSi$. |

Even more preferably, the polycrystalline

refractory metal silicide is selected from the listed silicides containing at least 25 but less than or up to 50 atomic % silicon.

The refractory polycrystalline metal silicide is advantageously tantalum silicide, $Ta_5Si_3$, which is taken by way of example to illustrate the invention. $Ta_5Si_3$ has the advantage that its melting point is 2440°C, highest of all known refractory silicides.

To enhance IR radiation, the thin film resistive heater of the micro-hotplate device can be coated with a semiconducting emission layer. This emission layer is advantageously plasma-etched black silicon having a needle-like structure.

Such emission layer has a transition between a low emissivity at a first temperature and a high emissivity state at a second temperature higher than the first temperature, enabling increasing the modulation amplitude of emitted power by alternating between the first temperature and the second temperature, which is particularly advantageous for pulsed IR sources.

Specific applications of the micro-hotplate device of the invention are in catalytic high temperature chemical sensors, micro-chemical reactors, micro-hot-fuel-cells or as infrared source.

Use of the claimed micro-hotplate is particularly advantageous at a temperature of 600°C or higher.

## Brief Description of the Drawings

The invention will be further described by way of example with reference to the accompanying drawings, in which:

Fig. 1 is a cross-section through a sandwich

structure encapsulating a thin film resistive heater of a device according to the invention;

Fig. 2 is a cross-section through another sandwich structure reinforced by a ceramic layer;

Fig. 3 is a cross-section along line A-A of Fig. 4, illustrating a micromachined silicon wafer supporting a membrane formed of a sandwich structure as shown in Fig. 2; and

Fig 4 is a schematic plan view of the wafer-supported device of Fig. 3, along the sectional plane corresponding to the thin film resistive heater.

## Detailed Description

Fig. 1 shows a free-standing thin film resistive heater 1 of polycrystalline refractory metal silicide advantageously tantalum silicide, $Ta_5Si_3$, encapsulated in a sandwich structure 5 between a protective top insulating layer 2a and a protective bottom insulating layer 2b, for example both made of tantalum oxide $Ta_2O_5$.

Fig. 2 shows a similar sandwich structure 5' mechanically reinforced by a ceramic supporting layer 3, in particular of $Si_3N_4$ (or low stress silicon nitride), this reinforcing layer 3 being located between the bottom protective layer 2b and the thin film resistive heater 1.

Figs. 3 and 4 show a micro-hotplate device comprising a sandwich structure 5 like that in Fig. 1 or 2, supported on a micromachined silicon substrate 4, with the bottom insulating layer 2b separating the thin film resistive heater 1 from the silicon substrate 4.

The silicon substrate 4 comprises a micromachined recess 6 that exposes the bottom insulating layer 2b through the recess 6, thereby liberating a thin, stress compensated, membrane 7 ($SiO_2$ + $Si_3N_4$) located in the

centre of the infrared source and supported on the silicon substrate 4 spanning the aperture provided by recess 6.

As shown in Fig. 4, the thin film resistive heater 1 is formed by a patterned layer in the membrane 7 of the sandwich structure 5' on silicon substrate 4. The membrane 7 constitutes a hot part of the device and the silicon substrate 4 constitutes a cold part of the device. The heater layer 1 has a narrow portion patterned in meander form and dimensioned to provide a given electrical resistance and to optimize thermal conductance between the membrane 7 and the substrate 4. As shown, the heater layer 1 is extended laterally by contact pads 8 located over the non-machined parts of the silicon substrate 4.

The bottom insulating layer 2b can be made by thermal oxidation of the silicon substrate 4. Then, the ceramic supporting layer 3 can be applied by sputtering or LPCVD (low pressure chemical vapor deposition).

Optionally, the underside of membrane 7 in the opening provided by recess 6 is coated with a black emission layer 9, which could be black gold or black platinum, but advantageously is needle-like black silicon obtained by plasma etching. The process for the formation of black silicon is the following. The backside deep etching through the silicon substrate 4 - preferentially dry etching - is stopped before reaching the thermal oxide of the membrane 2b. The remaining 10 to 50 $\mu$m of monocrystalline silicon are treated by dry etching with an increased oxygen pressure so as to achieve the needle type shape of the etched silicon. The emissivity of such needle-like black silicon at operating temperatures even up to 800°C is practically 100%, whereas platinum black has an emissivity of about 80% up to a maximum operating temperature of about 600°C.

Such black silicon layer has an emissivity of <90% at 400°C and practically 100% at 800°C, which makes it very advantageous in pulsed IR sources.

The polycrystalline tantalum silicide layer 1 can be deposited on the supporting layer 3 as a thin film by physical vapour deposition (PVD) processes, using for example a multi-target magnetron sputtering system.

Exemplary conditions for deposition of TaSi compounds are:

- Power applied on silicon target 100-200 W RF
- Power applied on tantalum target: 85-200 W (variable DC)
- Base pressure: $3.10^{-6}$ mTorr
- Argon flow rate: 25 sccm
- Deposition pressure: 8 mTorr
- Substrate temperature:setpoint/real: 650/550°C
- Substrate table rotation speed: 6 rpm
- Deposition time: 30 min.

Patterning of the conducting material 1 can be performed using ECR ion gun dry etching.

By way of example, the thin film resistive heater 1 is approximately 100 nm thick, 20 to 200 microns wide on the thin, stress-compensated membrane 7 located in the centre of the infrared source. The whole IR source can be about 6x6 $mm^2$, and the IR emitting membrane 7 ranges from 0.5x0.5 $mm^2$ to 2x2 $mm^2$. The meander structure stands on an approximately 2x2 $mm^2$ membrane. Instead of a meander structure further samples can be made as single-strip structures located on either 0.5x0.5 $mm^2$ or 1x1 $mm^2$ membranes.

The protective $SiO_2$ film 2a is sputter deposited. As illustrated in Fig. 3, the profile of this film matches the undelying meanders of layer 1.

Subjecting the refractory metal silicide during processing to temperatures above the crystallisation temperature (at least 600°C) is essential to achieve silicides of polycrystalline structure for the high temperature micro-hotplates of the invention.

Micromachining of the recess 6 takes place by standard anisotropic silicon wet etching or by dry etching for example with a gas containing $SF_6$.

The described IR micro-hotplate device shows outstanding performance. No measurable diffusion between the polycrystalline tantalum silicide layer 1 and the adjacent layers 2a,3 occurs at a temperature of 800°C during 12 hours. Indeed, neither the $SiO_2$ layer 2b nor the $Si_3N_4$ layer 3 showed diffusion of any species into or out of the conducting polycrystalline tantalum silicide thin film 1.

A constant average filament temperature of more than 1000°C is achieved during operation. Typically, a source as described with a surface of $2x2mm^2$ can be operated at an average temperature of more than 1000°C with an electrical power of 1200 mW.

The AC lifetime of a specimen IR source as described was around $1.10^6$ cycles at 10 Hz and 80% of the instant breakdown power.

Comparative tests were carried out with platinum, Ni-Cr alloy; pyrolised photoresist; SiC heavily doped with aluminium, TaSiN. Of the comparative examples, platinum showed the best performance.

With the infrared micro-sources according to the invention based on a PVD polycrystalline tantalum silicide thin film heating filament a constant average filament temperature of more than 1000°C is achieved during operation. This performance is outstanding

compared to that of standard platinum-based infrared sources (<600°C).

The composition of the thin film filament (thickness about 100 nm) is very close to that of stoichiometric $Ta_5Si_3$, when deposited by co-pulverisation from a tantalum target and a silicon target. It has been established that a 200 nm layer of $SiO_2$ offers a satisfactory high temperature oxidation barrier for the filament. It has been demonstrated that no measurable diffusion between tantalum silicide and the adjacent layers occurs. Indeed, neither $SiO_2$ nor $Si_3N_4$ thin films showed diffusion of any species into or out of the conducting TaSi thin film.

Crystallisation of $Ta_5Si_3$ occurs at a temperature of 650°C during the first heating starting from room temperature, leading to a drop of resistivity of more than 50% and to compensation of the compressive thermal stress by tensile stress due to film densification. Resistivity at ambient temperature after annealing around 900°C is about 60 μohm.cm, and a typical value of TCR is $50.10^{-4}K^{-1}$.

Observed device failure was always related to membrane breakdown, and the intrinsic temperature limit of the material was not reached. Membrane breakdown is either due to stress applied by the filament to the membrane or to thermal mismatch stress developed within the membrane.

Typically, a source with a surface of 2x2 $mm^2$ can be operated at an average temperature of 1000°C with an electrical power of 1200 mW. The maximum power for instant breakdown is about 2000 mW. AC lifetime of an IR source was tested up to $1.10^6$ cycles at 10 Hz and 80% of the instant breakdown power.

Many variations are possible within the scope of the appended claims.

## CLAIMS

1. A micro-hotplate device comprising a thin film resistive heater (1) made of a refractory metal silicide selected from silicides of tantalum, zirconium, tungsten, molybdenum, niobium and hafnium, the silicide having polycrystalline structure obtainable at a temperature above 600°C.

2. The micro-hotplate device of claim 1, further comprising a protective layer (2a, 2b) on the thin film resistive heater (1) made of electrically and thermally insulating material having low diffusability for oxygen or oxygen vacancies, protecting the polycrystalline refractory metal silicide from oxidation.

3. The micro-hotplate device of claim 2, wherein the protective layer is an oxide of tantalum, silicon or aluminium.

4. The micro-hotplate device of claim 2 or 3, wherein the thin film resistive heater (1) of polycrystalline refractory metal silicide is encapsulated in a sandwich structure between a protective top insulating layer (2a) and a protective bottom insulating layer (2b), and the sandwich structure is supported on a silicon substrate (4) with the bottom insulating layer (2b) separating the thin film resistive heater (1) from the silicon substrate (4).

5. The micro-hotplate device of claim 4, wherein the silicon substrate (4) comprises a micromachined recess (6) through which the bottom insulating layer (2b) is exposed, the sandwich structure forming a membrane (7) traversing the recess (6) on the silicon substrate (4).

6. The micro-hotplate device of claim 4 or 5, wherein the sandwich structure is mechanically reinforced by a ceramic supporting layer (3), in particular of $Si_3N_4$

or low stress silicon nitride, between the bottom protective layer (2b) and the thin film resistive heater (1).

7. The micro-hotplate device of any preceding claim, wherein the thin film resistive heater (1) is formed by a patterned layer in a membrane (7) on a substrate (4), the membrane constituting a hot part of the device and the substrate constituting a cold part of the device, the layer (1) being patterned to provide a given electrical resistance and to optimize thermal conductance between the membrane and the substrate.

8. The micro-hotplate device of any preceding claim, wherein the polycrystalline refractory metal silicide comprises from 25 to 67 atomic % silicon, and is selected from the following silicides of the given metals:

| | |
|---|---|
| Tantalum: | $Ta_3Si$, $Ta_2Si$, $Ta_5Si_3$, $TaSi_2$, |
| Zirconium: | $ZrSi_2$, $ZrSi$, $Zr_5Si_4$, $Zr_3Si_2$, $Zr_2Si$, |
| Tungsten: | $WSi_2$, $W_5Si_3$, |
| Molybdenum: | $Mo_3Si$, $Mo_5Si_3$, $MoSi_2$, |
| Niobium: | $Nb_5Si_3$, $NbSi_2$, and |
| Hafnium: | $Hf_2Si$, $Hf_3Si_2$, $Hf_5Si_4$, $HfSi$. |

9. The micro-hotplate device of any preceding claim, wherein the refractory metal silicide is polycrystalline tantalum silicide, $Ta_5Si_3$.

10. The micro-hotplate device of any preceding claim, wherein the thin film resistive heater is coated on its top and/or bottom side with a black emission layer, in particular of needle-like black silicon.

11. The micro-hotplate device of claim 10, wherein the

emission layer is a semiconductor exhibiting a transition between a low emissivity state at a first temperature and a high emissivity state at a second temperature higher than the first temperature, enabling increasing the modulation amplitude of emitted power by alternating between the first temperature and the second temperature.

12. A catalytic high temperature chemical sensor, a micro-chemical reactor, a micro-hot-fuel-cell or an infrared source, comprising a micro-hotplate device as claimed in any preceding claim.

13. Use of a micro-hotplate device as claimed in any preceding claim at a temperature of 600°C or higher.

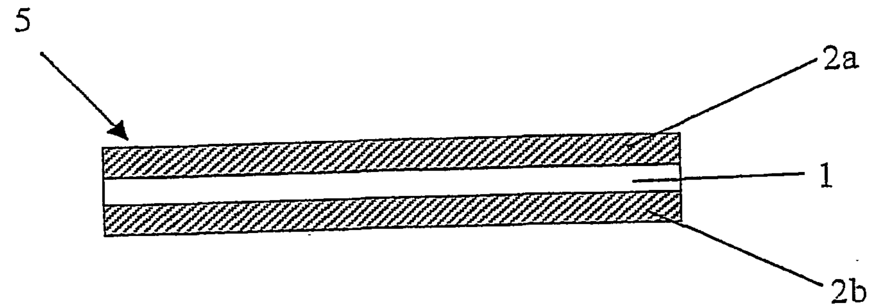



Figure 1

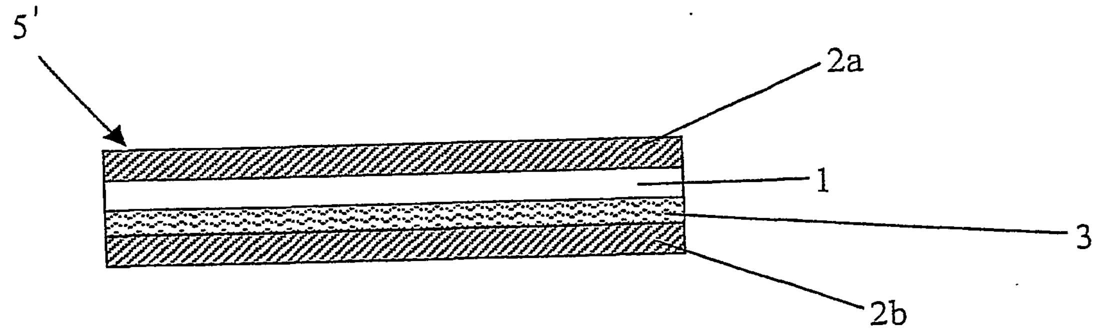



Figure 2

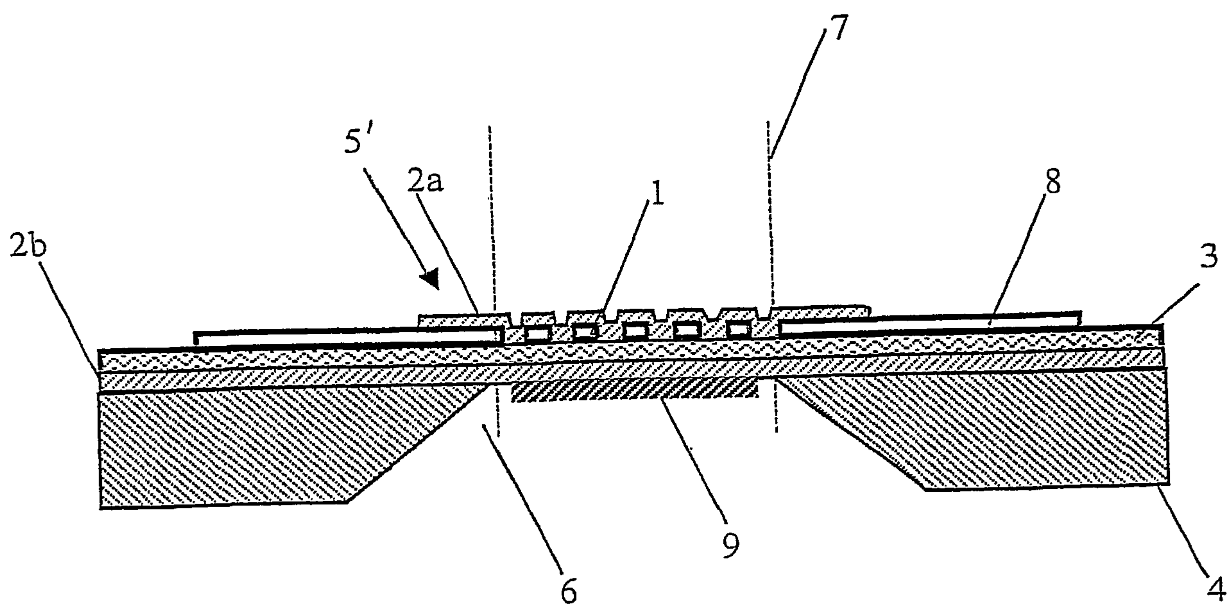



Figure 3

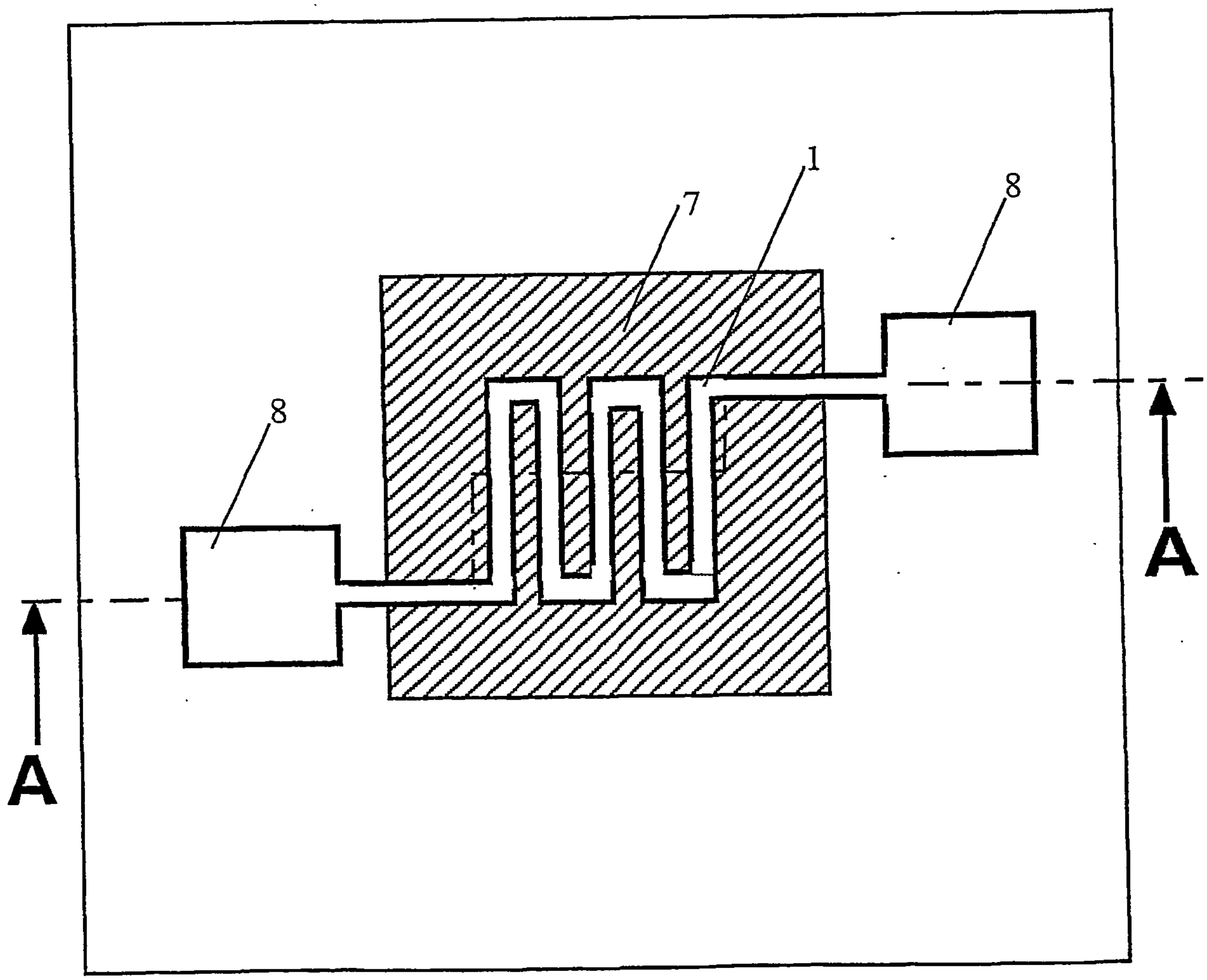



Figure 4

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 02/01024

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 7 H05B3/14

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H05B G01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 6 091 050 A (CARR) 18 July 2000 (2000-07-18) column 3, line 33 -column 39 column 3, line 52 - line 62 column 4, line 32 - line 60 column 5, line 28 - line 42 column 6, line 31 - line 34 | 1-4,7,9, 13 |
| Y | column 5, line 12 - line 16; figures 3A,3B,3C | 5 |
| Y | EP 0 776 023 A (VAISALA) 28 May 1997 (1997-05-28) figure 3A | 5 |

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 30 July 2002 | 06/08/2002 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31–70) 340–2040, Tx. 31 651 epo nl,<br>Fax: (+31–70) 340–3016 | Taccoen, J-F |

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 5 345 213 A (SEMANCICK)<br>6 September 1994 (1994-09-06)<br>column 4, line 28 - line 38<br>column 7, line 9 - line 11<br>column 7, line 34 - line 37<br>column 8, line 45 - line 49<br>column 10, line 27 - line 42<br>column 11, line 5 - line 13<br>column 3, line 59 -column 12, line 9<br>--- | 1 |
| A | US 5 464 966 A (GAITAN)<br>7 November 1995 (1995-11-07)<br>column 1, line 6 - line 9<br>column 4, line 39 - line 49<br>column 4, line 58 -column 5, line 9<br>column 6, line 19 - line 36; claim 15<br>----- | 1 |

| Patent document cited in search report | | Publication date | Patent family member(s) | | | Publication date |
|---|---|---|---|---|---|---|
| US 6091050 | A | 18-07-2000 | NONE | | | |
| EP 0776023 | A | 28-05-1997 | FI | 955657 | A | 25-05-1997 |
| | | | DE | 69615635 | D1 | 08-11-2001 |
| | | | DE | 69615635 | T2 | 11-07-2002 |
| | | | EP | 0776023 | A2 | 28-05-1997 |
| | | | JP | 9184757 | A | 15-07-1997 |
| | | | US | 5827438 | A | 27-10-1998 |
| US 5345213 | A | 06-09-1994 | AU | 6120294 | A | 24-05-1994 |
| | | | WO | 9410559 | A2 | 11-05-1994 |
| US 5464966 | A | 07-11-1995 | WO | 9410822 | A1 | 11-05-1994 |